

Can we prevent the “dead layer” formation at manganite interfaces?

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The present work theoretically studies the possibility to hinder the formation of a “dead” layer at the interfaces in manganite superlattices. We showed that this goal can be reached by using alkaline-earth simple oxides as alternating layers in very thin superlattices. Indeed, such alternating layer promotes the contraction of manganite layers at the interfaces and $d_{x^2-y^2}$ preferred e_g orbital occupancy, while Boltzman’s transport calculations show an increase in conductivity. This result hold for different manganites, different alkaline-earth simple oxides as well as different thicknesses of the two layers.

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Interfaces between perovskite oxides have been the subject of intense research over the last decade. The first reason is the outstanding properties discovered in such interfaces ; let us only cite the superconductivity discovered at the interface between two band insulators such as SrTiO₃ (STO) and LaAlO₃ [1]. Another reason is the potential applications of such properties. Manganite-based devices using tunnel junctions are actively studied for the design of spin valves or spin injectors. Such junctions present a high degree of spin polarization and robust magnetic properties at the interface between the manganite and the barrier. The main problem that has hindered the development of the such devices is the formation of a so-called “dead-layer” [2, 3], below a critical distance to the interface. In such layers the magneto-transport properties are strongly depressed. The present paper proposes a possible solution to this critical problem with not only a set of criteria to design appropriate barriers, but also a detailed study of a realistic example.

Manganites are known to be ferromagnetic metals over a large range of their phase diagram, and to present colossal magneto-resistance effects. Indeed, the record value is of over 14 orders of magnitude in resistivity change under magnetic field [4]). Their transport and magnetic properties are controlled by small atomic displacements, allowing potential pathways to tune their properties using interfaces in very thin films and heterostructures (see for instance Ref. 5–8, and Ref. 9 for a recent review). Unfortunately, a loss of magnetization and metallicity, also called “dead layer”, is observed over a thickness of few unit cells (u.c.) at the interface of ferromagnetic manganites, such as La_{2/3}Sr_{1/3}MnO₃ (LSMO) or La_{2/3}Ca_{1/3}MnO₃ (LCMO), and most perovskite substrates or combined layers [2, 3]. This “dead layer” phenomenon has been the subject of many interpretations such as (i) homogeneous substrate strain [10], (ii) electronic and/or chemical phase separation [11] related to structural inhomogeneities at the interface [12]

or uncontrolled stoichiometry [13], (iii) manganese e_g orbital reconstruction that may induce C-type antiferromagnetism [14, 15] and can be attributed to a weak delocalization at the interfaces [16]. The first hypothesis is incoherent with the relaxation rate of the substrate strain, shown to be larger than 1000 Å [11], while a drastic change in the transport properties [3, 13, 14] is observed at the STO interface, for films thinner than a few u.c. In this work we would like to work with perfect interfaces, we will thus not consider the consequences of imperfectly grown interfaces and focus on the last hypothesis of enhanced d_{z^2} occupancy at the interface. Such a behavior was attributed to an energetic lowering of the d_{z^2} orbital over the $d_{x^2-y^2}$ at the interface, due to a weak delocalization of the former through the interface [16].

Ferromagnetic manganites (and related heterostructures) of general formula La_{1-x}A_xMnO₃ (A a divalent cation, x in the approximate range $0.2 < x < 0.45$) crystallize in a ABO₃ perovskite structure [22, 23], with the Mn occupying the B site. The Mn atom is thus in an octahedron environment, which induces an energetic splitting of the Mn 3d orbitals into a t_{2g} — threefold degenerated — low energy set, and a e_g — twofold degenerated — high energy one (ideal case). Moreover, the Mn atoms are in a mixed valence ionic state (Mn^{3+x}), with a $3d^{4-x}$ high spin orbital occupancy. As a result, the two e_g orbitals, d_{z^2} and $d_{x^2-y^2}$, are partially occupied by $1 - x$ electron which may delocalize (the d_{z^2} electrons along the **c** direction and the $d_{x^2-y^2}$ ones in the (**a,b**) plane). This delocalization is energetically very favorable, but will only occur when the spins of neighboring Mn ions are ferromagnetically aligned. In such a case the delocalization energy gain overcomes the antiferromagnetic exchange interaction between localized ions, and imposes a ferromagnetic ordering (double exchange mechanism) [17].

In bulk materials the e_g electrons are shared between the two orbitals with equivalent occupancies. It results

in magnetic ordering and delocalization occurring in all directions. In very thin films, however, the out-of-plane direction, \mathbf{c} , spans only over a few u.c., and thus the thermodynamic limit is only obtained in the in-plane, (\mathbf{a}, \mathbf{b}) , directions. It is thus of crucial importance for the magnetic and transport properties to maximize the $d_{x^2-y^2}$ orbital occupancy, responsible for the in-plane delocalization and thus magnetic and transport properties.

When an interface “dead layer” is present, the d_{z^2} electrons of the manganite delocalize in the empty d_{z^2} orbitals of the substrate or of the alternating layer (typically SrTiO_3 , BaTiO_3 or similar compounds). Even if weak (about one or two tenth of an electron [16]), at the interfaces this delocalization energetically favors the d_{z^2} orbital occupancy over the $d_{x^2-y^2}$ one. It results in a Jahn-Teller distortion of the MnO_6 octahedron, with a splitting of the e_g degeneracy [18] ($\varepsilon_{z^2} < \varepsilon_{x^2-y^2}$). The in-plane delocalization is thus hindered (at least by carrier density reduction). Consequently, the characteristics of the “dead layer” phenomenon appear, (reduced ferromagnetic spin arrangement and conductivity [3, 19]). Such a Jahn-Teller distortion induces a small increase of the \mathbf{c} parameter [16, 20], that can be fully attributed to the delocalization mechanism at the interfaces, as strain effects tend to reduce \mathbf{c} . Indeed, on a STO substrate, manganites such as LSMO or LCMO are under tensile strain ($\mathbf{a}_{\text{STO}} = 3.905\text{\AA}$ [21], $\mathbf{a}_{\text{LSMO}} = 3.880\text{\AA}$ [22], $\mathbf{a}_{\text{LCMO}} = 3.86\text{\AA}$ [23] yielding a 1% strain on LSMO and 2% on LCMO), known to favor a reduction of \mathbf{c} . In order to prevent the formation of a “dead layer”, one thus needs to interface the manganite with an alternating layer material hindering the delocalization between the different layers.

The purpose of this work is thus to investigate, using first-principle calculations, possible candidates for such alternating layers. We will focus on LSMO-based heterostructures over a SrTiO_3 substrate.

The first idea that may come to mind, is to use alternating layers with totally-filled d -shells, and a tetragonal structure. Indeed, the latter was shown to be crucial in order to prevent the rhombohedral distortion in the manganite layer, but rather favor a tetragonal one [18]. Let us remember that a tetragonal distortion, associated with a \mathbf{c} parameter contraction, allows an enhancement of the $d_{x^2-y^2}$ orbital occupancy and thus of the desired properties. One could therefore think of materials such as the BaSnO_3 compound. Unfortunately, our test calculations on such hetero-structures exhibited a weak electron delocalization, from the Sn filled d_{z^2} orbitals towards the Mn partially occupied ones, very similar to what we observed in our calculations on BTO/LSMO [18] or STO/LSMO heterostructures (that exhibit a JT distortion of ~ 1.04 in the interface layer, a dominant d_{z^2} occupancy and a weak d_{z^2} delocalization in the Ti orbitals.). This delocalization is associated with an increase of the Mn d_{z^2} orbital occupancy, and a Jahn-Teller distortion. One can thus

expect such hetero-structures to exhibit a “dead layer” phenomenon.

Another way to prevent the inter-layers delocalization of the LSMO Mn d_{z^2} orbitals is to totally avoid d orbitals, in the alternating layer material. The requirement for the alternating layer should thus be i) no d orbitals, ii) a tetragonal or cubic structure, and iii) a compound allowing perfect epitaxy with the manganite layer. Fulfilling all those requirements are the simple alkaline-earth oxides, and more specifically the BaO compound. Indeed, the mismatch between BaO and LSMO is only of 0.7%, and between BaO and the STO substrate 0.3%. Of course the epitaxy imposes a BaO unit cell ($Fm\bar{3}m$ cubic group [24]) rotated in-plane by an angle of 45° [25], compared to the manganite unit cell (see figure 1).

We thus studied, using first-principles calculations, $[\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_n[\text{BaO}]_p$ superlattices on a STO substrate, alternating a few u.c. of manganite and of simple Barium oxide. Superlattices with other alkaline-earth oxides were also investigated to see whether the results are resilient to a change in the alternating layer, despite their unrealistic strain values [26].

We performed geometry optimizations for the different superlattices, using periodic density functional calculations. Since epitaxial films normally follow the structure of the substrate, we imposed to our optimizations to keep the substrate in-plane lattice constants (optimized using the same computational parameters). The alkaline-earth oxides are strong insulators, while the manganite layers are expected to be metallic, one thus needs to choose a functional that properly positions the metal Fermi level with respect to the insulator gap. We used the B1WC hybrid functional [27], that was specifically designed to properly treat both gaps and weak distortions, two key components in the present systems. The calculations were done using the CRYSTAL package [28], with the basis sets and effective core pseudopotentials (ECP) of ref. 29. As the LSMO A-site cations disorder is difficult to treat within periodic calculations, we run a set of calculations with different orderings, using true atoms or average ones. The average ions were modeled as in reference 18, that is using ordered cations ECPs but with averaged effective nuclear charges. The effect of these average charges is to hinder possible electronic localization induced by the cation orders. Unless specified, we will only present results that are independent of the cation order or model. Finally we used a $\sqrt{2}a \times \sqrt{2}a \times c$ unit cell in order to allow octahedra rotations and in-plane antiferromagnetic (AFM) ordering (see figure 1).

We first studied the $[\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_3[\text{BaO}]_6$ superlattice, using all 6 cations models and different magnetic orders ; that is ferromagnetic (FM), A-type AFM (in-plane FM and out-of-plane AFM), C-type AFM (in-plane AFM and out-of-plane FM) and G-type AFM (in-plane and out-of-plane AFM).

Notice that in what follows we consider superlattices

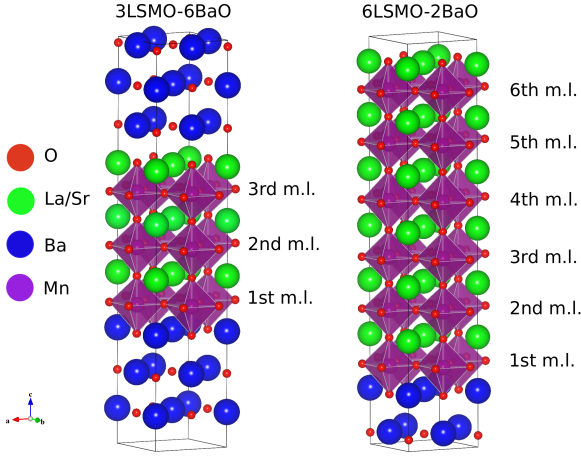


FIG. 1: (color online) Schematic representation of the $[\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_3[\text{AO}]_6$ and $[\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_6[\text{AO}]_2$ superlattices.

with stoichiometric layers yielding, in most cases, asymmetric interfaces as it would be in real heterostructures. As it will be discussed in the last Section, this has however no direct impact on our conclusions.

Our calculations showed that the magnetic ground state always imposes a FM in-plane order and a total net magnetic moment. The two out-of-plane magnetic arrangements are quasi-degenerate within DFT error bars. Indeed, the energy difference per LSMO u.c. (or equivalently per Mn), between FM and A-type AFM orders, is in average 8 meV/u.c., with a mean deviation of 16 meV. This is smaller than the room temperature ($k_B T \sim 25$ meV). Whether the DFT ground state is the FM or the A-type AFM configuration depends on the specific cation ordering. The in-plane AFM ordered states are much higher in energy, ranging between 130 meV and 210 meV above the ground states.

Figure 2 pictures the statistics of both the Jahn-Teller distortion (JTd) (measured as $d_{\text{OO}}/a - 1$, with d_{OO} the out-of-plane O-(Mn)-O distance) and c/a (c being the perovskite A-sites distances) as a function of the e_g orbitals-occupancies ratio. Results are given for each mono-layer and the two possible ground states. Before analyzing the results let us keep in mind that the two interface layers are non equivalent, since one corresponds to a (La/Sr,O)-(BaO) interface and the other to a (MnO₂)-(BaO) interface.

One sees immediately that all three layers are compressed along the c direction, except for the central layer in two AFM calculations. Similarly, the Mn-octahedra of the interface mono-layers are compressed along c and display a dominant $d_{x^2-y^2}$ orbital occupancy, favorable to the searched magnetic semi-metal behavior. Only the central monolayer exhibits sometimes an elongation of the Mn-octahedra, with a dominant d_{z^2} occupancy. This behavior is the exact opposite of what is found in

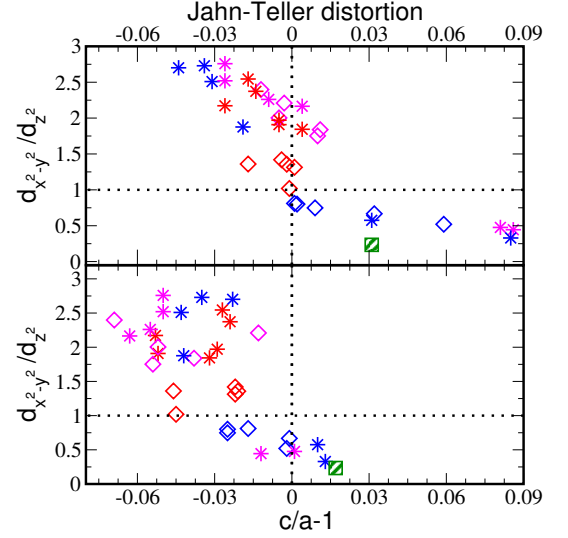


FIG. 2: (color online) $\eta(d_{x^2-y^2})/\eta(d_{z^2})$ ratio of the $d_{x^2-y^2}$ and d_{z^2} orbitals Mulliken occupancies in each mono-layer as a function of the Jahn-Teller distortion (JTd) (measured as $d_{\text{OO}}/a - 1$, with d_{OO} the out-of-plane O-(Mn)-O distance) and of c/a (c being measured as the perovskite A-sites distance). Red and pink symbols refer to the interfacial mono-layers, blue symbols to the central ones. Diamonds are for the FM order and stars for the A-type AFM one. The green dashed squares show the experimental values of LSMO over STO for 6 m.l. thin films exhibiting a dead layer. The Jahn-Teller distortion and c/a ratios are extracted from the cumulative displacements in Ref. 20 and the $\eta(d_{x^2-y^2})/\eta(d_{z^2})$ ratio is extracted from linear dichroism experiments of Ref. 14. Bulk LSMO corresponds to the cross point between the dashed lines.

$[\text{LSMO}]_3[\text{BTO}]_3$ superlattices [18, 30], in which the interface layers are elongated with a dominant d_{z^2} occupancy, responsible for the dead layer behavior. One should also point out that octahedra rotations are essentially negligible in these hetero-structures (rotation values less than 1°).

The fact that the FM and A-type AFM orders are found so close in energy tells us that, in real systems such superlattices may present one or the other spin arrangement as the ground state, according to the specific cation disorder. In any way at room temperature both state can be expected to be occupied with similar probabilities. Our results thus show that such superlattices should display a net total magnetization (even though reduced compared to the FM state), and more importantly a large magnetic moment for the interface layers. Concerning the transport properties we computed the conductivity tensor for the $[\text{LSMO}]_3[\text{BaO}]_6$ and the $[\text{LSMO}]_3[\text{BaTiO}_3]_3$ systems using the Boltztrap [31] code. Figure 3 clearly shows a strong increase in the in-plane conductivity for the system with BaO alternating layers. The dominant $d_{x^2-y^2}$ orbital occupancy at the interfaces, supported by the conductivity

calculations, lead us to think that using simple oxides as alternating layers is indeed a promising way to prevent the “dead layer” phenomenon.

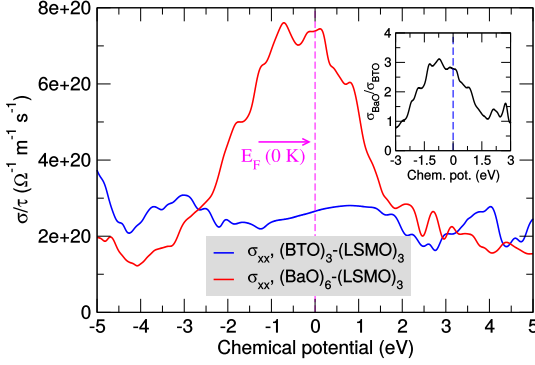


FIG. 3: Transport calculations on $[\text{LSMO}]_3[\text{BaO}]_6$ and $[\text{LSMO}]_3[\text{BaTiO}_3]_3$ systems. The dotted line represent the Fermi level.

One can however wonder if this conclusion will remain valid if one increases the size of the manganite layer. In order to check this point we increased the size of the LSMO layer to 6 mono-layers, and performed the calculations for one typical cation configuration. To keep this calculation to a reasonable size, we needed to simultaneously decrease the BaO layer thickness. We thus first checked whether such a reduction would affect the results. For this purpose we run test calculations on the preceding superlattice with only two mono-layers of BaO (*i.e.* on $[\text{LSMO}]_3[\text{BaO}]_2$). These calculations showed a similar behavior to the calculations with 6 BaO mono-layers, and thus validate 2 BaO mono-layers model.

Our calculations on the $[\text{LSMO}]_6[\text{BaO}]_2$ superlattices showed that the ground state again imposes in-plane ferromagnetism. The spin arrangement in the c direction displays a $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$ pattern (“**uudduu**”) with a total net magnetization for the system. This ground state is again very close in energy to the FM state and the A-type AFM state. The latter does not however correspond to a full AFM state, since it exhibits a non null net total magnetization of about 1/10 of an electron per Mn atom.

The dominant e_g orbital occupancy in the different LSMO mono-layers is found qualitatively independent of the out-of-plane spin ordering (see table I for an example). Indeed, as in the $[\text{LSMO}]_3[\text{BaO}]_6$ calculations, the mono-layers at the interfaces are contracted and strongly dominated by the $d_{x^2-y^2}$ orbital occupancy. In fact only the inner most mono-layer is still elongated and dominated by d_{z^2} orbital occupancy. As it can be seen in Table I, the Mn magnetic moments and the amplitude of the Jahn-Teller distortion exhibit a strong correlation. The Mn-octahedra in the inner most mono-layer exhibit a strong elongation and the largest Mn magnetic moment. This specificity of the inner most mono-layer is responsible for the non-vanishing total magnetization in

the A-type AFM state. These results show that, when in-

LSMO mono-layer	e_g orb. $d_{x^2-y^2}$	spin pop. d_{z^2}	$c/a - 1$	JTd	μ_{Mn}
1	0.46	0.32	-0.032	0.017	3.55
2	0.47	0.24	-0.028	-0.034	3.43
3	-0.46	-0.25	-0.021	-0.038	-3.45
4	-0.30	-0.74	0.013	0.070	-3.89
5	0.48	0.22	-0.027	-0.035	3.44
6	0.50	0.29	-0.043	-0.012	3.57

TABLE I: Mülliken spin population of the Mn e_g orbitals, c/a ratio, JTd (Jahn-Teller distortion) and μ_{Mn} (Mn magnetic moment) in the $[\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3]_6[\text{BaO}]_2$ ground state of one typical cation order. Values for the two other low energy states (FM and A-type AFM) are qualitatively equivalent.

creasing the thickness of the LSMO layer, one essentially increases the thickness of the interface layers and not of the central one. The former being contracted along c and dominated by $d_{x^2-y^2}$ orbital occupancy, it confirms that the use of BaO alternating layers hinder the formation of a “dead layer” at the LSMO interfaces.

Finally we checked whether this result is resilient to a change in the simple oxide and manganite compounds. We thus performed a set of calculations using BaO, SrO and MgO as alternating layers, and LSMO or LBMO as manganite layers ($[\text{La}_{2/3}\text{A}_{1/3}\text{MnO}_3]_3[\text{BO}]_6$), for a typical cation disorder model [26]. Table II summarizes the e_g orbital occupancies for those calculations. One may

	LAO mono-layer	e_g orb. $d_{x^2-y^2}$	spin pop. d_{z^2}
LBMO-BaO	1	0.44	0.29
	2	0.38	0.54
	3	0.51	0.26
LBMO-BaO ($P4/mmm$)	1	0.48	0.27
	2	0.24	0.66
	3	0.48	0.27
LSMO-SrO	1	0.48	0.26
	2	0.40	0.52
	3	0.48	0.26
LSMO-SrO ($P4/mmm$)	1	0.48	0.25
	2	0.40	0.53
	3	0.48	0.25
LSMO-MgO	1	0.35	0.17
	2	0.23	0.70
	3	0.60	0.26
LBMO-MgO	1	0.35	0.17
	2	0.24	0.70
	3	0.59	0.32

TABLE II: Mülliken spin population of the Mn e_g orbitals in the $[\text{La}_{2/3}\text{A}_{1/3}\text{MnO}_3]_3[\text{BO}]_6$ ground state (A=Sr, Ba ; B=Ba, Sr, Mg). The shown example was chosen as the cation ordering associated with the lowest ground state energy.

notice that the $(\text{LBMO})_3(\text{BaO})_6$ and $(\text{LSMO})_3(\text{SrO})_6$ superlattices have in theory equivalent interfaces, unlike all the other superlattices we studied. One sees in table II

that this symmetry is kept in the $(\text{LSMO})_3(\text{SrO})_6$ superlattice. Indeed, the two calculations with and without imposed symmetry yield equivalent results within error bars. For the $(\text{LBMO})_3(\text{BaO})_6$ superlattice however, this is not the case. Indeed, a spontaneous symmetry breaking occurs along the \mathbf{c} axis, associated with a small energetic stabilization ($37 \text{ meV} \simeq 430 \text{ K}$) per LBMO u.c. This induces a symmetry breaking in the e_g orbitals occupancies as can be seen in table II. Nevertheless, all manganite interface mono-layers are favoring a $d_{x^2-y^2}$ occupancy over a d_{z^2} one, as was the case for the $(\text{LSMO})_n(\text{BaO})_p$ compounds. This result thus seems to remain valid independently of the manganite compound and of the simple oxide chosen for the alternating layer.

As a conclusion one may recall that thin films and superlattices of $[\text{La}_{2/3}\text{A}_{1/3}\text{MnO}_3]$ ($\text{A}=\text{Sr}, \text{Ca}$) manganite compounds, over an SrTiO_3 substrate, have been extensively studied in the hope to find a good material for electronic and spintronics applications. Indeed, on such an STO, the LSMO is under tensile strain, so one is entitled to expect that the elastic energy will favor a contraction of the mono-layers along the \mathbf{c} direction. Due to the degeneracy of the e_g orbitals, such a contraction would have enhanced the occupation of the $d_{x^2-y^2}$ over the d_{z^2} and thus the ferromagnetic and metallic behavior through the double exchange mechanism. Unfortunately the formation of a non-magnetic and insulating layer (called “dead layer”) at the interface prevents to reach this goal. This “dead layer” originates in a weak delocalization of the Mn d_{z^2} orbitals in the empty Ti ones. The energy gain in this phenomenon overvalues the elastic energy loss [16]. As a consequence a preferred occupancy of the Mn d_{z^2} orbitals associated with an elongation (along the \mathbf{c} direction) of the interface mono-layers takes place.

In this paper, we theoretically studied different possibilities to hinder the interface delocalization using suitable alternating layers in superlattices. Our first principle calculations show that superlattices alternating manganite and alkaline-earth simple oxides efficiently prevent inter-layer delocalization, promote mono-layers contraction at the interfaces and a preferred $d_{x^2-y^2}$ occupancy over the d_{z^2} one, and finally strongly increase the in-plane conductivity. Our studies show that this result should hold for different manganite and alternating layer thicknesses. One can thus reasonably expect that such superlattices may present the long searched magnetic and electric properties.

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